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W. Ternent Cooke

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Experiments on the Chemical Behaviour of Argon and Helium.

By W. Ternent Cooke, D.Sc.

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Historical and Introductory.—The discoverers of argon, Rayleigh and Ramsay, showed[*] that when subjected to very severe chemical treatment the gas failed to combine with any other element. Later on Collie and Ramsay also showed[†] that helium resembled argon in being chemically inactive. Moissan[‡] and Berthelot[§] both carried out experiments with argon, but neither obtained real proof of any power of argon to enter into chemical combination.

It has always been assumed that if union of argon or helium with any other element occurred the action would be strongly endothermic, and experiments have always been framed in such a way as to impart to the system a plentiful supply of energy.

There being a sufficient quantity of both gases at disposal, it was deemed desirable to make further experiments on the chemical behaviour of argon and helium, and to work at temperatures higher than those which hitherto had usually been employed. Then, again, it was desired to obtain, if possible, evidences of partial combination, and to this end experiments on the vapour densities of various elements in both gases, at temperatures between 1200° and 1300° C., were carried out.

When a known weight of a substance is vaporised in a given volume of gas, which is chemically inert towards the substance, we can calculate the density of the vapour, if we know the final temperature and pressure of the gaseous mixture. If, however, the gas of the substance combines totally, the resulting compound will have, generally, a greater density than that of the vapour of the substance. High values, then, for the density may be taken as indicative of chemical combination, even if the combination be but partial. The method used in this work was to obtain values for the densities of various elements in inert gases, and to compare these values with those found in the same apparatus when argon or helium was the gas used. High

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[*] 'Phil. Trans.,' A, 1895, p. 231.

[†] 'Roy. Soc. Proc.,' vol. 60, p. 53.

[‡] 'Compt. Rend.,' vol. 120, p. 966.

[§] 'Compt. Rend.,' vol. 120, pp. 581, 1316; and vol. 129, pp. 71, 378.

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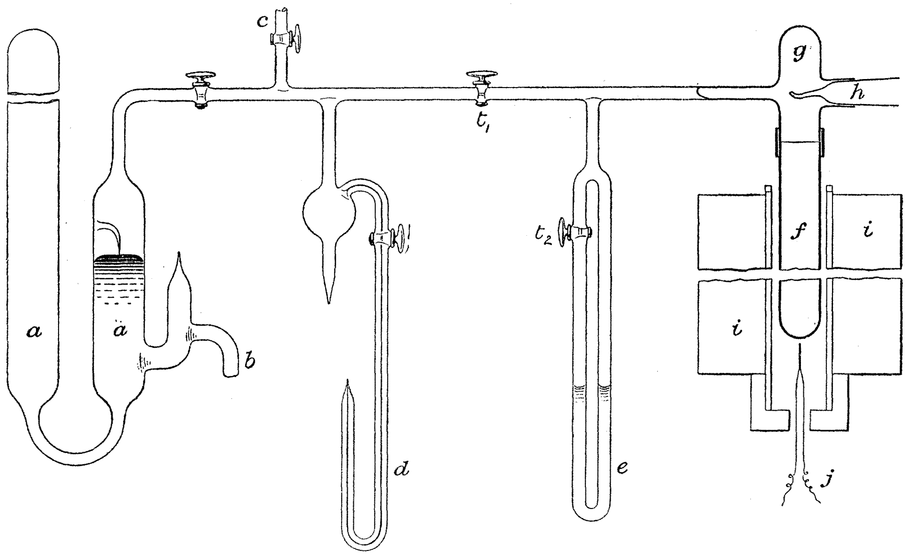
values for the densities were considered as evidence of the occurrence of chemical combination.*

The Apparatus.—Heat was supplied by means of an electrical resistance oven, and temperatures were determined by means of a thermocouple of platinum—rhodioplatinum—which was calibrated by the method of fixed points. The main portions of the apparatus, which is essentially a Victor Meyer apparatus, is shown in the sketch :—



a is a constant volume manometer, connected at *b* to a movable reservoir of mercury.
The tubing at *c* leads to a Töpler pump.
d is a capillary U-tube, used for introducing gas into the apparatus.
e is a differential manometer.
f is a silica glass tube, 25 cm. long, 12 mm. internal diameter, and about 1·5 mm. thick in the walls ; 15 to 16 cm. of its length projected into the oven.
g is a glass head-piece, which was secured to the silica tube by means of thick rubber tubing. This rubber joint was surrounded with mercury.
h is a stopper working in a ground glass joint. The stopper is shaped like a spoon at one end, and serves to hold the substance previous to its being dropped into the silica tube.
i is an electric resistance oven.
j is a thermo-couple.
t_1 and t_2 are taps.

Method of Working.—Suppose all the air has been pumped out of the apparatus, that the temperature is sufficiently high, and that a weighed amount of substance is in the spoon, ready to be dropped. Helium, say, is admitted into the apparatus through the capillary U-tube, *d*, and the pressure of the gas obtained by means of the absolute manometer. The tap, t_1, is closed, the level of the liquid in the left limb of the differential manometer noted, the tap, t_2, closed, and the contents of the spoon tipped out. The level of the liquid in the left limb of the differential manometer rises, and the reading of this is taken. The temperature is then immediately read. All the necessary readings having been thus ascertained, the helium is pumped out, and the oven allowed to cool.

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* *Note by Sir William Ramsay.*—It has been noticed ever since the discovery of argon that metals such as platinum, magnesium, and aluminium, used as negative electrodes in

Calculation of the Density.—It will be seen that the volume of the vapour is determined indirectly, *i.e.*, by noting the increase of pressure it occasions. To find the volume, consider first the differential manometer. At the beginning of the experiment the pressure, p_1, is equal in both limbs. Call V_1 the volume of the closed, V_2 the volume of the open limb. When the substance vaporises the alteration of the level of the liquid in both limbs is equal. The volume of the closed limb becomes V_3, and the pressure p_3, where $p_3 = p_1V_1/V_3$. In the open limb the pressure becomes p_4, and the volume V_4. Now $p_4 = p_3+2h$, where h is the displacement of the level of the liquid, supposing it to be mercury. If, now, the mass of the gaseous contents of the open limb had remained constant, it would have occupied, under the pressure p_4, a volume V_2p_1/p_4 instead of V_4. The volume of the

a Plücker tube, "splashed" much more readily in that gas than in oxygen, nitrogen, or hydrogen, at low pressures. After the discovery of the other inert gases, this observation was a matter of almost daily occurrence. An explanation of this remarkable phenomenon may be found in the supposition that the energy imparted to the gas at its surface of contact with the electrode is sufficient to cause chemical combination between the two in that region. On leaving the electrode, however, the supposed endothermic compound may be imagined to dissociate, and the gas may be liberated, with simultaneous deposit of the metal on the walls of the tube. Similar experiments with zinc, cadmium, antimony, and mercury have shown that they, too, when made the cathode in an atmosphere of one of these gases, volatilise much more easily than in nitrogen or hydrogen. It has also been often noticed that on filling a vacuum tube with an indifferent gas, in which operation the gas has stood in contact with mercury, the spectrum of mercury is seen in the vacuum tube more frequently than when diatomic gases are submitted to the same treatment. These facts afford presumptive evidence that chemical combination occurs to a limited extent between metals and the indifferent gases.

Again, in repeating Berthelot's experiment of submitting argon and helium to the silent discharge in contact with benzene vapour and mercury, it was observed that, so long as nitrogen was present, the glow in the annular space between the electrodes had the usual faint violet colour; but as soon as all nitrogen had entered into combination, the tube glowed with a brilliant green light. Examined with the spectroscope, this showed only the lines of mercury. Here again there is presumption that absorption of energy causes combination between the inert gas and mercury, forming a compound more volatile than mercury, but decomposing almost as soon as formed.

vapour at this pressure is, therefore, $V_4 - V_2 p_1/p_4$. Calculating for a pressure p_1, we have for the volume of the vapour V_v

$$V_v = \frac{p_4 V_4}{p_1} - V_2. \qquad \text{(A)}$$

By weighing the mercury contained between any two points in the manometer tube it was found that every millimetre of length corresponded to a volume of 0·0093 c.c. Hence,

$$V_3 = (V_1 - 0{\cdot}0093h),$$
$$V_4 = (V_2 + 0{\cdot}0093h),$$

h being expressed in millimetres.

Again

$$p_3 = \frac{V_1 p_1}{V_3} = \frac{V_1 p_1}{(V_1 - 0{\cdot}0093h)}$$

and

$$p_4 = (p_3 + 2h) = \frac{V_1 p_1}{(V_1 - 0{\cdot}0093h)} + 2h.$$

Inserting these values into equation A, we get

$$V_v = \frac{[V_1 p_1/(V_1 - 0{\cdot}0093h) + 2h]\,[V_2 + 0{\cdot}0093h]}{p_1} - V_2. \qquad \text{(B)}$$

V_1 was determined by finding the weight of mercury required to fill the space, and V_2 by measuring the amount of dry air contained in that volume of the apparatus.

We have now the volume in cubic centimetres of the vapour given by a known weight of substance, the volume being determined for a pressure p_1 and a temperature $t°$ C. The density of the vapour, taking H = 1, is given by the equation

$$D = \frac{760 \times 1000}{0{\cdot}899 \times 273} \times \frac{g(t + 273)}{V_v p_1}, \qquad \text{(C)}$$

where g = weight of substance in grammes and 0·0899 gramme is the weight of 1 litre of hydrogen at N.T.P.

When the apparatus was used to determine the vapour density of zinc in nitrogen, the values found were from three to four times too great. An error in this direction is to be expected, since the relative dimensions of the various parts of the apparatus were unsuitable for an apparatus intended to give absolute values. The volume of the heated part should be many times greater than that of the cooler part, whereas in the present case about one-third of the volume, that is the volume of the open limb of the differential manometer, was at the highest temperature. Moreover, diffusion and mixing is very rapid at high temperatures. Since, however, in the present case, differential results only are required, comparative figures were obtained by determining the density of the substance used in some indifferent gas besides in argon and helium. For the sake of convenience, figures are reduced to absolute values. The reducing factor is obtained by calibrating the apparatus, using as a standard the mean of the values found for zinc in an atmosphere of nitrogen. The mean of five determinations gave the value 111. This value multiplied by 0·293 gives 32·5, which is the vapour density of zinc when hydrogen is taken as unity.* Hence, to reduce to its absolute value, the density of a vapour was multiplied by 0·293.

There is another fact to be considered. In a light gas like helium, diffusion is much more rapid than in argon or nitrogen, and higher values for the density are likely to be obtained in the lighter gas. For the sake of a juster comparison, a series of determinations was made in hydrogen, if the nature of the substance allowed. Hence, in making comparisons, values found in argon are compared with those found in nitrogen, and values in helium with those in hydrogen.

Materials Used.—The argon and helium were carefully purified in the usual way by passage over heated lime and magnesium mixture, and also over heated copper oxide. Spectroscopic examination showed that each gas was practically pure, a trace of hydrogen only being present.

"Atmospheric" nitrogen was used; it was obtained by burning phosphorus in dry air, and finally subliming part of the phosphorus in the nitrogen left.

Hydrogen was made from electrolytic zinc and pure sulphuric acid.

All the gases used were thoroughly dried before use by passage over phosphorus pentoxide.

Of the substances whose vapour densities were required, ordinary samples were taken, the purest at hand being selected. The substances used were zinc, cadmium, mercury, sulphur, selenium, and arsenic. The number of elements which could be used was limited. The temperatures were not high enough to vaporise heavy metals such as lead or tin. Antimony, bismuth, and tellurium just begin to vaporise.† Bismuth, too, attacks silica slightly. Phosphorus presented experimental difficulties which could not be overcome. The use of potassium, etc., calcium, etc., and magnesium is out of the question, since heated silica is at once attacked by them. The size of the apparatus enabled only very small amounts of the substances to be used, and less than 3 milligrammes were sufficient. Weighings were made by the method of swings. Weights were calculated to 0·01 milligramme, and are accurate to within 2 per cent.

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* V. Meyer, 'Ber.,' vol. 19, p. 3295.

† *Cf.* Blitz and Meyer, 'Zeit. Phys. Chem.,' vol. 4, pp. 259, 263.

Table of Results.

Weight in milli-grammes.	Tempera-ture in ° C.	Density found.	Density corrected.
	Zinc in nitrogen (standard).		
1·54	1270	117·1	—
1·25	1284	106·5	—
1·09	1271	107·8	—
1·45	1308	110·7	—
1·54	1294	112·8	—
		111·0	32·5
	Zinc in argon.		
1·51	1285	130·0	38·1
1·63	1299	132·0	38·7
1·33	1278	119·0	34·9
1·63	1278	111·0	32·5
2·28	1268	130·0	38·1
		124·5	36·4
	Zinc in hydrogen.		
1·13	1250	114·2	33·4
1·27	1280	107·3	31·4
1·82	1310	118·2	34·6
1·77	1268	132·2	39·6
1·67	1276	123·6	36·2
2·15	1276	148·0	44·3
		124·4	36·4
	Zinc in helium.		
1·37	1284	125·8	36·9
1·46	1280	121·0	35·4
1·46	1277	129·0	37·8
1·63	1267	120·1	35·2
1·53	1283	114·5	33·5
		122·1	35·8
	Cadmium in nitrogen.		
1·93	1281	191·2	56·0
1·23	1275	183·8	53·8
2·16	1196	198·4	58·1
		191·1	56·0
	Cadmium in argon.		
1·64	1292	189·8	55·6
2·04	1289	186·6	54·7
2·6	1237	178·2	52·2
		184·86	54·2
	Cadmium in hydrogen.		
1·81	1260	169·1	49·5
2·1	1252	180·9	53·0
1·97	1234	162·1	47·5
		170·7	49·9
	Cadmium in helium.		
1·68	1288	192·7	56·5
1·77	1273	198·9	58·3
2·16	1260	184·8	54·1
2·07	1266	189·8	55·6
		191·5	56·1
	Mercury in nitrogen.		
2·81	1291	370·55	108·67
2·41	1265	389·95	114·26
2·38	1190	312·36	91·52
2·35	1288	335·46	98·16
		352·1	103·2
	Mercury in argon.		
1·86	1308	409·9	120·1
2·4	1287	324·4	95·0
2·04	1287	482·3	141·3
2·49	1300	358·0	104·9
		393·6	115·3
	Mercury in hydrogen.		
1·73	1266	380·1	111·4
2·35	1278	340·9	99·9
		360·5	105·6

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Table of Results—*continued.*

Weight in milli-grammes.	Tempera-ture in ° C.	Density found.	Density corrected.
Mercury in helium.			
2 ·07	1286	356 ·7	104 ·5
2 ·07	1284	352 ·4	103 ·2
3 ·02	1244	371 ·6	108 ·9
2 ·45	1278	335 ·9	98 ·4
4 ·25	1246	384 ·4	112 ·6
1 ·945	1282	463 ·7	135 ·9
		377 ·5	110 ·6
Arsenic in nitrogen.			
1 ·82	1286	332 ·15	97 ·3
2 ·41	1280	281 ·1	82 ·4
2 ·205	1271	362 ·95	106 ·3
1 ·71	1295	298 ·7	87 ·5
3 ·02	1203	425 ·4	124 ·6
		340 ·1	99 ·65
Arsenic in argon.			
1 ·92	1263	341 ·43	100 ·0
1 ·88	1291	325 ·77	95 ·5
		333 ·6	97 ·7
Arsenic in helium.			
1 ·96	1288	343 ·0	100 ·5
1 ·92	1183	322 ·7	94 ·5
2 ·215	1202	350 ·2	102 ·6
2 ·32	1261	339 ·4	99 ·4
		338 ·3	99 ·1
Sulphur in nitrogen.			
1 ·57	1292	101 ·8	29 ·8
1 ·4	1230	101 ·5	29 ·7
1 ·81	1291	160 ·7	47 ·1
2 ·2	1246	106 ·7	31 ·2
		117 ·7	34 ·5

Weight in milli-grammes.	Tempera-ture in ° C.	Density found.	Density corrected.
Sulphur in argon.			
1 ·44	1303	114 ·9	33 ·7
1 ·3	1286	114 ·2	33 ·4
		114 ·5	33 ·55
Sulphur in helium.			
1 ·4	1276	107 ·6	31 ·5
1 ·236	1284	102 ·7	30 ·1
1 ·41	1244	104 ·9	30 ·8
1 ·52	1300	113 ·6	33 ·3
1 ·68	1250	146 ·3	42 ·9
		115 ·0	33 ·7
Selenium in nitrogen.			
1 ·92	1277	227 ·6	66 ·7
2 ·49	1249	239 ·6	70 ·2
1 ·925	1273	230 ·6	67 ·6
		232 ·6	68 ·1
Selenium in argon.			
1 ·63	1275	245 ·3	71 ·9
2 ·1	1278	252 ·3	73 ·9
1 ·88	1288	227 ·4	66 ·6
		241 ·7	70 ·8
Selenium in helium.			
2 ·01	1302	275 ·1	80 ·6
2 ·1	1286	209 ·0	60 ·3
2 ·25	1280	251 ·4	73 ·6
		245 ·2	71 ·8

Discussion of Results.—Taking the elements separately and comparing the densities in argon with those in nitrogen, and the densities in helium with those in hydrogen, it will be seen that there is a distinct tendency of zinc and argon to combine, the density being 12 per cent. higher in argon than in nitrogen. With helium there is no tendency to combine.

Cadmium and argon show no tendency to combine, but in helium the density is 12·4 per cent. higher than in hydrogen. The values for mercury are very irregular. The irregularity is due mainly to the fact that when the globule of mercury, which is very small, is placed in position for dropping, it is at a temperature high enough to melt sulphur, and for some time is exposed to a vacuum. Under these conditions it undoubtedly suffers loss in weight. The mean values show that there is a tendency for the metal to combine with argon and with helium.

In the case of arsenic, of sulphur, and of selenium, it is, of course, impossible to obtain values in hydrogen, since chemical combination takes place. Arsenic and sulphur show no tendency to combine with either gas, while selenium exhibits a slight tendency to combine with both.

I desire to tender my best thanks to Professor Sir William Ramsay, who suggested the research to me, and besides kindly placing at my disposal the argon and helium necessary for the experiments, gave me every encouragement in the work.

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